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CHEMICAL HAZARDS ASSOCIATED
WITH THE HANDLING OF URETHANES:
A LITERATURE SEARCH

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13. ABSTRACT (Maximum 200 words) This report presents the findings of a literature search documenting the hazardous materials to which workers may be exposed when handling hot, burning, or abraded polyurethanes. The topic hazardous materials is divided into two areas: (1) Chemical hazards identified in the work atmosphere and traceable to starting materials used in the manufacture of urethanes. An extensive list of chemicals associated with the manufacture of urethanes [such materials as the prepolymer (isocyanates), cure agents (MOCA), catalysts (amines), and solvents (chlorinated hydrocarbons)] was compiled for use by abstracting services conducting the search. (2) Chemical hazards identified in the smoke produced when urethanes are thermally decomposed. A list of key words (e.g., health and fire hazards, smoke, and toxic substances--urethanes) was compiled for use by the abstracting services when conducting the literature search. In this report, discussion of hazardous materials consists of quotations, authoritative comments, and citations from specific OSHA/NIOSH regulations. Pertinent references are given.				
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CHEMICAL HAZARDS ASSOCIATED WITH THE HANDLING OF URETHANES: A LITERATURE SEARCH

INTRODUCTION

The purpose of this report is to present the findings of a literature search whose goal was to document the hazardous materials to which workers may be exposed when handling hot, burning, or abraded polyurethane.

To facilitate conducting the literature search, the topic *hazardous materials* was divided into two areas:

- Chemical hazards identified in the worker atmosphere and traceable to starting materials used in the manufacture of urethanes. An extensive list of chemicals associated with the manufacture of urethanes [such materials as the prepolymer (isocyanates), cure agents (MOCA), catalysts (amines), solvents (chlorinated hydrocarbons)] was compiled for use by abstracting services conducting the search.
- Chemical hazards identified in the smoke produced when urethanes are thermally decomposed. A list of key words (e.g., health and fire hazards, smoke, and toxic substances--urethanes) was compiled for use by the abstracting services when conducting the literature search.

The following abstracting services were used in preparation of this report: Chem Abstracts (American Chemical Society), DIDS--Document Information Directory System (NIOSH), and the Defense Technical Information Center (DTIC). In addition to the search conducted by the abstracting services, a personal review of the literature was conducted. Journals included in this review were: Analytical Abstracts, and the annual reviews of the Journal of the American Industrial Hygiene Association, the Annals of Occupational Hygiene, the Journal of Occupational Medicine, the American Review of Respiratory Diseases, and the the British Journal of Industrial Medicine. Pertinent articles in other journals were reviewed as they were uncovered during the search. The time period covered in the review was, in most cases, 1970 to 1987.

The contribution of one publication to the content of this report must be acknowledged. Near the end of the literature search in preparation for this report, "Review of the Literature on the Gaseous Products and Toxicity Generated from the Pyrolysis of Rigid Polyurethane Foams" [1] was published by the National Technical Information Service (NTIS). This paper was prepared by two researchers (M. Paabo and B.C. Levin) at the Center for

Fire Research, National Bureau of Standards. References cited in their paper were used in preparation for the section on hazards in smoke in this report.

Discussion of hazardous materials will consist of quotations, authoritative comments, and citations from specific OSHA/NIOSH regulations. Pertinent references are listed.

CHEMICAL HAZARDS ASSOCIATED WITH THE MANUFACTURE OF POLYURETHANES

Isocyanates

In the manufacture of polyurethanes, the most hazardous chemicals are the isocyanates. Although several monoisocyanates have important chemical reactions, the following diisocyanates will be discussed primarily because of their importance in the literature (of hazardous materials) and because of the relevancy to the immediate problem: toluene diisocyanate (TDI); methylene bis phenylisocyanate (MDI), also called diphenylmethane diisocyanate; and polymethylene polyphenylisocyanate (PAPI--a registered trademark of the Upjohn Co.) [2-9].

It is clear from the literature review that isocyanates, particularly TDI, represent a major source of concern for workers handling hot, burning, or abraded polyurethane. Before discussing the specifics of this hazard, a general review of the hazardous nature of isocyanates will be presented [2-9].

In general, all isocyanates exhibit the unusual characteristic of a low oral toxicity with a high chronic inhalation toxicity. Isocyanates are irritating to the skin and the mucous membranes; with the skin conditions ranging from localized itching to more or less widespread eczema. Eye affections are less common and, although lacrimation is often found, conjunctivitis is rare [2-9].

The most common and also most serious problems resulting from exposure to isocyanates are those affecting the respiratory system. The direct irritant or toxic response is due to triggering the normal protective mechanisms of the upper respiratory tract and mimics other respiratory irritants. The symptoms, depending on total dose, appear four to eight hours after onset of exposure and may persist for some time. The symptoms are those associated with increased protective mechanisms: increased secretion, cough, pain on respiration and, if severe enough, some restriction of air movement due to a combination of secretions, edema, and pain [2-9].

A second type of response to exposure to isocyanates is host generated or controlled, is truly allergic, and is referred to in the literature as "TDI Asthma." It is not to be expected on initial exposure but usually develops after a time in the work area. It may masquerade as a cold or mild hay fever until a full-blown asthmatic-like attack occurs. Sensitization and "allergic" symptoms occur in approximately 17% of the general population. Seven percent of those involved demonstrate hay fever symptoms and 5.7% are classified with other allergies. There is no cross

sensitization to other unrelated materials; however, cross sensitization between isocyanates has been documented. Exposure by individuals with existing respiratory diseases (chronic bronchitis, emphysema, or tuberculosis) to isocyanates is likely to cause aggravation. The literature suggests [2-9] that once an individual becomes sensitized (develops TDI Asthma) they are sensitized for life. Woolrich [8] states that "proper management of these sensitized workers with interruption and discountinuation of any further exposure prevents the occurrence of any residual effects or recognizable impairment."

In general, exposure by individuals to various concentrations of isocyanates in air is likely to have the following effects [2-9]:

- 0-0.02 ppm: there is little danger of a reaction to the isocyanates;
- 0.02-0.1 ppm: there is the potential of sensitivity symptoms appearing in a small portion of the population;
- 0.1-1.0 ppm: irritation of the respiratory tract and mucous membranes will occur; and
- 1.0 ppm and greater: there is potential for acute toxic effect.

To put this data [2-9] into perspective, tests performed on humans indicate that the least detectable odor of TDI is apparent at about 0.2-0.4 ppm. Irritation of the nose and throat occurs (for TDI) at about 0.5 ppm, and an appreciable odor is recognized at 0.8 ppm. These data indicate that if TDI can be detected, the maximum acceptable concentration has been exceeded and a hazardous condition exists [2-9].

The Threshold Limit Value (TLV) for MDI or TDI vapor has been set by OSHA at 0.2 ppm of air. It is a maximum value not to be exceeded [2-9]. NIOSH has set the TLV for diisocyanates at 0.005 ppm for a time-weighted average (TWA) for up to a 10-hour workshift, 40-hour work week, and 0.02 ppm as a ceiling concentration for any 10-minute sampling period [2-9]. The 5-ppb TWA and the 20-ppb TLV are somewhat controversial and have been under review by a number of researchers; some believe that these levels are too high and should be lowered to 1-2 ppb. Diem and co-workers [10] conducted a five-year longitudinal study of workers employed in a TDI-manufacturing plant and concluded that "the nonsmoking, high cumulative exposure group (defined as an average time of exposure of 28.2 minutes above the current TLV) will experience an excess average decline of 38 ml/yr in important pulmonary function tests." This translates to a 1.5-liter decline in a 40-year working lifetime. Robins and co-workers [11] contend that this level of decline is not satisfactory and that the Diem data suggests a lowering of the NIOSH-recommended standard to "at least 1 to 2 ppb."

Toluene Diisocyanate

This substance is most widely used in industry and produces the greatest number of pathological manifestations because of its high volatility (vapor pressure), and because it is often used in considerable

concentrations. The effects of inhalation and effects on the skin and eyes have been previously discussed. Animal experiments indicate that the toxicity of TDI when swallowed is not high. It is believed that swallowing TDI probably would not be fatal in humans but would result in severe irritation and probable corrosive action on the stomach. Mutagenicity and carcinogenicity tests for TDI were negative [2-9].

Diphenylmethane Diisocyanate

This substance (MDI) is less volatile and its fumes become harmful only when the temperature approaches 75°C. The effects of inhalation or ingestion, effects on skin and eyes, mutagenicity, and carcinogenicity are similar to those for TDI [2-9].

Polymethylene Polyphenylisocyanate

PAPI is manufactured to be approximately 50% MDI and 50% higher molecular weight MDI oligomers and has an average composition of a trifunctional material. It is a dark amber, viscous liquid with very low volatility and a slower reactivity rate than many common aromatic diisocyanates. The effects of inhalation or ingestion, the effects on skin and eyes, mutagenicity, and carcinogenicity resemble those of MDI from which it is derived [2-9].

The potential hazard posed by isocyanates (specifically TDI) in the vapors produced by urethanes that are thermally decomposed will be discussed later in this report.

Carcinogenic Amines

Free MOCA [(4,4'-Methylene Bis(2-Chloroaniline))]

Virtually all of the MOCA consumed in the US is believed to be used as a curing agent for isocyanate containing polymers; and it is reported to be the most widely used agent for curing liquid castable polyurethane elastomers suitable for molded mechanical articles and for potting and encapsulating purposes. Since it is normally used in less than stoichiometric amounts in the production of polyurethane elastomers cured with MOCA, unreacted MOCA is not normally thought to be present in the final material. Since the curing agents are melted before mixing into the elastomer formulations, MOCA could find its way into the worker environment and onto the surface of cured urethane stock and into the waste gases and water from plants where it is being used [2-9].

MOCA exhibits the general toxicity characteristics of aromatic amines (i.e., cyanosis and methemoglobinemia). There is sufficient evidence for the carcinogenicity of MOCA in experimental animals. MOCA was found to be carcinogenic in mice and rats after dietary administration, producing vascular, liver, and lung tumors. It produced distant tumors (liver and lung cancers) in rats after subcutaneous injection. On the other hand, close medical surveillance has disclosed no adverse effect on workers engaged in the manufacture of MOCA although it and its metabolites have been found in their urine. Some workers have been exposed to MOCA for up to 18 years. In a plant manufacturing MOCA, a worker was splashed in the

face with molten material. The subject complained of a sick stomach but apparently recovered rapidly, without incident. MOCA has been given an A2 designation; meaning an industrial substance suspect of carcinogenic potential to humans [2-9].

NIOSH recommends that employee exposure to MOCA in the workplace be controlled so that no worker will be exposed at concentrations in excess of 3 micrograms per cubic meter of air determined as a time-weighted average (TWA) concentration for up to a 1-hour work shift, 40-hour workweek, over a work lifetime [2-9]. The American Conference of Governmental Industrial Hygienists lists a TLV-TWA of 0.02 ppm (approximately 0.22 mg/m³) [2-9].

Since MOCA is readily absorbed through the skin, all skin contact with it must be prevented [2-9].

Other Amines

Analysts at the Uusimaa Regional Institute of Occupational Health in Helsinki, Finland have developed a liquid chromatographic method for aromatic isocyanates and carcinogenic amines in the worker atmosphere. Among the hazardous materials this method is designed to detect are 2,4-diaminotoluene (2,4-TDA) and 4,4'-diaminodiphenylmethane (MDA). Both materials result from the hydrolysis of the corresponding isocyanate: 2,4-TDA from TDI, and MDA from MDI [12-17].

Other Material Discussed in the Literature

Urethane Foam Dust

Because of the widespread use of urethane foam in the construction and insulation industries, Laskin and co-workers [18] and later, Stemmer and co-workers [19] initiated inhalation studies for freshly generated urethane foam dusts generated during cutting operations. Laskin observed squamous cell carcinomas and pulmonary lesions (including centrilobular emphysema) in rats and hamsters exposed to dust five days a week for six weeks. Stemmer [19] observed inflammation and macrophage activity initially. Fibrosis developed after 6 months, nodular scars and perifocal emphysema were seen after 12 months, and papillary adenoma in a major bronchus was observed in four rats after 12 months of exposure to freshly generated urethane foam dust.

Potential hazards posed by particulates in smoke generated when urethanes are thermally decomposed will be discussed in the next section of this report.

CHEMICAL HAZARDS IDENTIFIED IN THE SMOKE PRODUCED WHEN URETHANES ARE THERMALLY DECOMPOSED

Since 1970, a large number of articles have been published that describe scientific studies designed to assess the smoke and fire hazards associated with urethanes. The focus of these studies has been the types of urethane materials used industry-wide. Industry statistics show that urethane foams have found wide-spread use for building insulation, thermal insulation in domestic and commercial refrigeration, and cushion material

in the furniture and bedding industries. Rigid urethane is also used for structural portions of furniture and for decorative paneling. The volume of articles on this subject suggests serious concern for worker/end-user safety.

It is important to note that rigid and flexible foams are used in most studies dealing with the thermal decomposition of urethanes. To date, no articles have been reviewed which deal with the mechanisms of decomposition or decomposition products from nonfoam, composite urethanes. As will be discussed later, the literature suggests [1, 18, and 20-26] that the decomposition products generated from the thermal decomposition of a urethane foam are dependent upon the composition of the urethane in question.

The literature also suggests [1] three possible mechanisms for the thermal decomposition of urethane foam. The mechanisms are:

- Dissociation of the urethane to an isocyanate and an alcohol;
- Dissociation of the urethane to form an olefin, primary amine, and carbon dioxide; and
- Dissociation of the urethane to form a secondary amine and carbon dioxide.

General equations for each dissociation mechanism are shown in Fig. 1.

The following factors, thought to influence the decomposition of urethane foams, have been described in the literature [1]:

- Conditions of thermal degradation (temperatures of decomposition, oxygen availability (oxidative or inert degradation), and ventilation).
- Type of foam (flexible or rigid).
- Formulation of the urethane (isocyanate type, and presence of filler, surfactant, blowing agent, and/or fire retardant in the formulation).

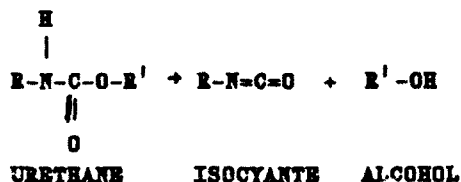
Most studies [1, 18, and 20-26] designed to identify decomposition mechanisms/products have been performed under laboratory conditions using small-scale pyrolysis and a controlled atmosphere. Inert atmosphere conditions (in a gas chromatograph, thermal analyzer, mass spectrometer, or gas chromatograph-mass spectrometer) appear to be favored for studies designed to identify breakdown products of toxicological interest. Breakdown products from real fire situations are best simulated using flaming or smoldering conditions in a ventilated, oxidative atmosphere. Paabo and Levin conclude "that many of the products (of breakdown) are the same regardless of whether the atmosphere was inert or oxidative".

The following paragraph summarizes conclusions drawn from the literature [1, 18, and 20-26] relative to the thermal decomposition of urethane foam: At relatively low temperatures (300°C), the flexible foams decompose by the depolymerization reaction (Figs. 1 and 2) resulting in a "yellow smoke" (mainly polymeric isocyanates) and a residue (mainly polyol). When heated at elevated temperatures (over 800°C), the "yellow

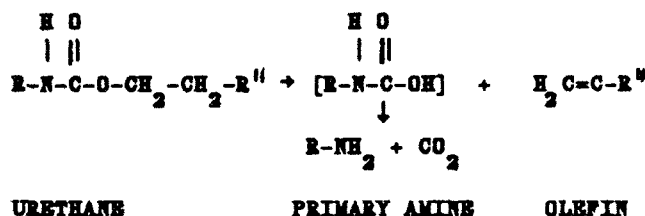
smoke^a condenses to form HCN and various other nitrogen-containing compounds. When the yellow smoke or the foam is heated to 1000°C, about 70% of the nitrogen in the original foam is converted to HCN. More than 100 compounds have been identified in the vapors produced from the thermal decomposition of urethanes; however, HCN and carbon monoxide (CO) appear to be the predominant toxicants. The generation of both HCN and CO appears to increase with increasing temperature. At 1000°C, the highest yields reported in the literature were 26.5 mg/g for CO and 73.3 mg/g for HCN.

The remainder of this report will be devoted to specific hazards to which workers might be exposed when urethanes are thermally decomposed.

A. DISSOCIATION TO ISOCYANATE AND ALCOHOL



B. FORMATION OF A PRIMARY AMINE AND OLEFIN



C. FORMATION OF A SECONDARY AMINE

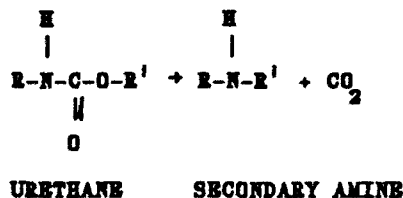


Fig. 1 - Thermal decomposition mechanisms for polyurethanes

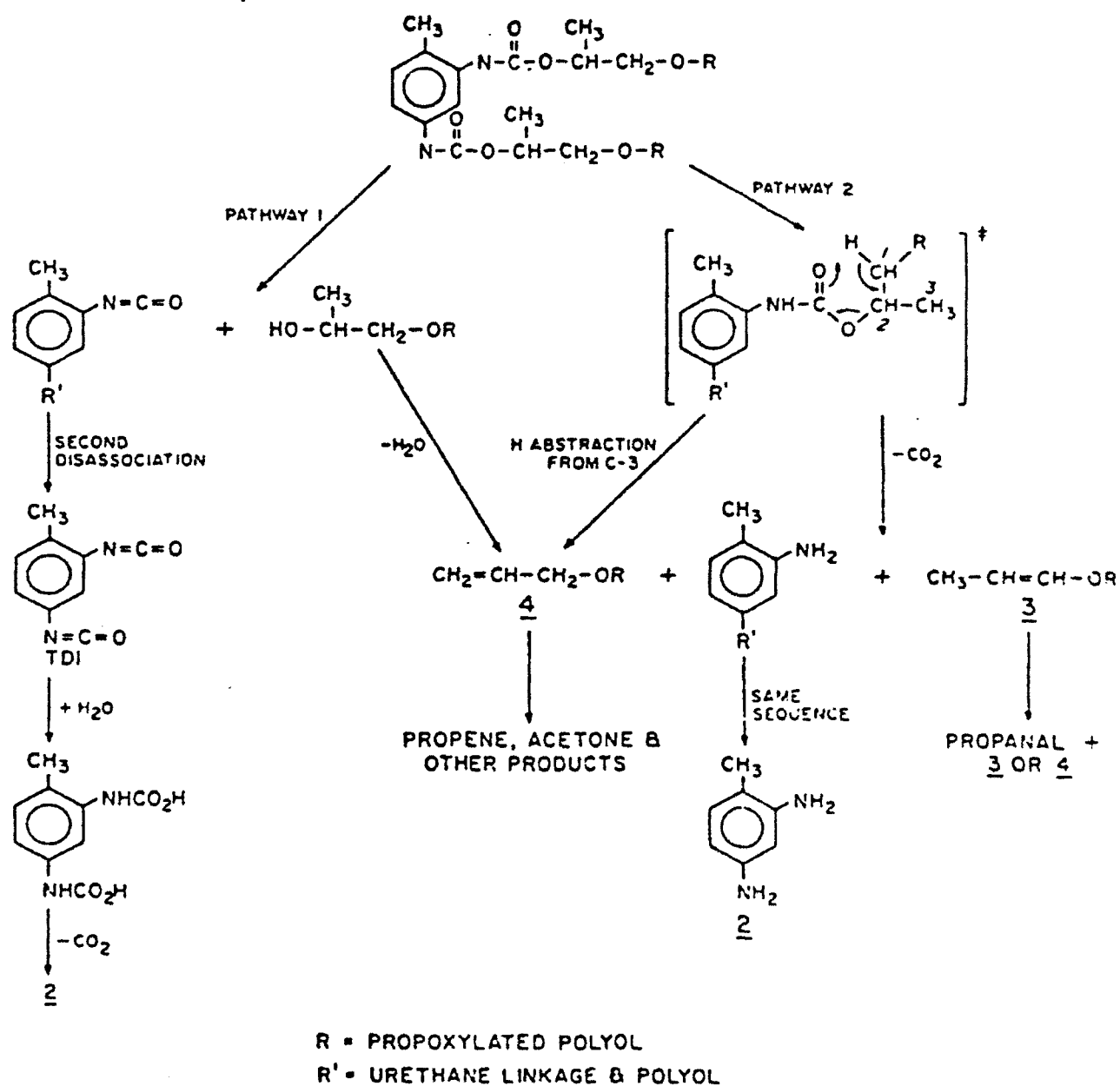


Fig. 2 - Reaction scheme for pyrolysis of flexible-urethane foam.

Isocyanate Hazard from Handling Hot Urethanes (Low Thermal Stress)

The review of the literature documents the generation of TDI when urethane foam slabstock is heated to temperatures as low as 250°C. The following literature citations support this observation:

- In 1979, Hardy and Devine [27] described industrial processes which resulted in the generation of TDI, the most relevant of which is the "hot-wirecutting of urethane foam slabstock. The authors state that the problem is especially acute when workers carry against their chests fresh-cut sections still warm and emitting fumes.
- Hileman and associates [28] have confirmed the generation of TDI when flexible-urethane foams were subjected to degradation under inert pyrolysis conditions using a GC-MS and chemical ionization mass spectroscopy. Pyrolysis products were identified and quantified at four pyrolysis temperatures (300, 500, 750, & 1000°C). Hileman has proposed a decomposition mechanism explaining the production of TDI from cured urethane foam. The mechanism (Pathway #1) is shown in Fig.2. The strongest evidence in favor of Pathway #1 results from pyrolysis at 300°C from which pyrolysis products are propene, water, and TDI. Traces of ethanal and propanal were also observed. This suggests that at 300°C the major route of decomposition is disassociation of the urethane to produce TDI, then dehydration of the alcohol followed by cleavage to produce propene. The question of water reacting with the isocyanate is a possibility since substantial amounts of carbon dioxide were identified. The amine produced by reacting the isocyanate and water would not be volatile enough to pass through the GC column. The presence of the trace amounts of propanal seems to indicate that at 300°C there is only a small contribution of Pathway #2. As the temperature is raised above 300°C, both of these pathways are operative. It should be noted that each of the mechanisms leads to a common intermediate (#4--propene, acetone, and other products). Ingredients used to prepare the flexible urethane foam used in this study are found in Table 1.
- Wolley [29] has documented the production of free TDI from the thermal decomposition of flexible urethane foam at temperatures as low as 250°C. Thermal decomposition was carried out in both nitrogen and oxygen atmospheres. A GC was used to confirm the presence of TDI in the volatile decomposition products. Wolley found that "at low temperatures (200-300°C), there was a rapid and complete loss of TDI from a TDI-polypropylene oxide polymer as a yellow smoke leaving a polyol residue." In air, maximum yields (1.15 and 0.7 weight percent conversion for the polyester and polyether foams, respectively) are recorded at 300°C for the polyester foam and at the slightly lower temperature of 250°C for the polyether material.
- Finally, Rogers and Ohlenmiller [30] have published kinetic studies on the decomposition of a flexible polyurethane foam based on toluene diisocyanate and a polyether polyol of propylene oxide using a thermogravimetric technique (TGA). In dry nitrogen the decomposition proceeds in two overall steps. At the end of the first step, which

follows a diffusion-controlled rate law, the cellular structure collapses to a viscous tarry liquid. The resultant tarry liquid gasifies in the second overall step by a random nucleation mechanism. The gaseous product will most likely be the isocyanate used to prepare the urethane. In describing the sequence of events, the author's purpose was to derive those kinetic parameters that provide the best fit to the experimental and theoretical curves for the thermal decomposition of flexible polyurethane foam. In this way, an empirical description of the decomposition process at heating rates comparable to those found in smoldering combustion would be assured.

Table 1 - Ingredients in urethane formulation.*

FORMULATION (parts by weight)	
Propoxylated triol (3000 mw)	100.00
Water	3.19
Silicone surfactant	0.90
Bis-dimethylaminoethyl ether	0.08
Stannous octoate	0.45
Toluene diisocyanate (80/20 mixture of 2, 4/2, 6 isomers)	46.19

* Formulation used by Hilemand and associates [18] to conform generation of TDI from heated urethanes.

HCN and CO Generation from Thermal Decomposition of Urethanes (High Thermal Stress)

Several authors [1, 21, and 31] document the observation that HCN appears to be the predominant nitrogen-containing compound produced when rigid polyurethane foam is decomposed at high temperatures in an inert atmosphere. In one study, at 1000°C the yield of HCN from four rigid foams varied between 38 and 73 mg/g which indicated that 27.8 to 42.8% of the nitrogen was recovered as HCN. CO can be produced under inert conditions from urethane foam since it contains oxygen in its molecular structure. Miller [32] documented the evolution of CO from the rigid urethane foam increased from 0.29 mg/g at 500°C to 2.8 mg/g at 750°C to 26.5 mg/g at 1000°C. These studies document the generation of both CO and HCN from rigid polyurethane increases with increasing temperature.

Production of volatile combustion products from the thermal decomposition of rigid urethane foam in air (oxidative conditions) has been studied over a wide range of temperature and ventilation conditions. The following is a brief summary of relevant articles:

- Michal [20] evaluated the generation of CO from a number of rigid urethane foam materials under different oxygen concentrations in order to simulate real fire conditions in which the oxygen concentration in the atmosphere can vary widely. Michal concluded that, "the CO content in the combustion products of the rigid urethanes studied was shown to increase with increasing temperature."

- Ashida and co-workers [21] studied the generation of HCN from urethane foams as a function of specific chemical formulation. Specially prepared rigid and flexible urethane foams based on TDI and PAPI formulations were pyrolyzed in both air and nitrogen. With PAPI-based foams, the quantity of HCN evolved during decomposition in air appeared to be related to the nitrogen content of the foam. This observation was not found in the TDI-based foams that produced much less HCN than the PAPI-type foams. Ashida concluded that HCN generation was dependent upon the formulation of the urethane and that oxygen was necessary for HCN generation.
- Evolution of HCN depends not only on the atmosphere and chemical formulation but also the temperature of decomposition. Michal [22] conducted a systematic study of HCN concentrations generated from rigid urethane insulation foam under oxidative conditions at controlled temperatures ranging from 600 to 1200°C. In air, the yields of HCN ranged from 15.8 mg/g at 600°C to 48.1 mg/g HCN at 1200°C.
- Lee and co-workers [23] conclude that blowing agents can contribute compounds of toxicological concern to the fire atmosphere during thermal decomposition of rigid urethane foam.
- Most studies examined for this report conclude that, with one exception, there have been no significant differences noted between the toxicities of the thermal decomposition products from fire-retarded and non-fire-retarded rigid urethane foams. An unusual toxic effect was observed in laboratory animals when a laboratory-formulated PAPI/propoxylated trimethylpropane rigid foam containing the reactive fire retardant 0,0-diethyl-N,Nbis-(2-hydroxyethyl) aminomethyl phosphate was decomposed under nonflaming conditions. A highly toxic bicyclic phosphate ester was produced in significant quantities at 500°C. Foams of this composition are no longer manufactured in England [1].

Particulate Combustion Products (High Thermal Stress)

Some of the complex organic compounds generated during flaming or non-flaming combustion do not remain as gaseous products in the fire atmosphere but condense onto smoke particulates. Joseph and Browner [24] thermally decomposed a foam under smoldering conditions and identified many compounds in the particulate fraction of the smoke. They found many potentially toxic compounds in the smoke not normally observed in the volatile fraction. This study points to the extremely complex nature of the combustion products from urethanes and reinforces the importance of the particulate nature of the smoke.

RECOMMENDATIONS

The science of hazard assessment has improved considerably over the 17-year period surveyed for the report. For example, defining the toxicants present in smoke in a "fire" situation is reasonably straightforward. Early in the review period, description of the conditions

for producing the toxicants and a clear definition of the toxic effects on humans was not straight forward. Complicating the problem was the lack of clear-cut results of laboratory tests defining the conditions under which chemical hazards were generated. In the late 1970's, Wysocki [28] made the following observation, "There are many tests; however, the test results are not predictable from one type of laboratory to another. This is most serious because laboratory tests generally do not predict performance in a "real-fire" situation." Much has changed in the past eight years. The National Bureau of Standards, National Engineering Laboratory has established a Center for Fire Research. On the academic scene, the University of Utah has established the Flammability Research Center. Researchers at these institutions have made major advances in standardizing the tests used to determine flammability of materials, and have defined new standards for assessing the toxicity of combustion products.

Research into the area of chemical hazards associated with urethanes is ongoing. Findings of this research can be found in current journals. To be meaningful, the contents of this report should be periodically revised to reflect current knowledge concerning the chemical hazards described.

The purpose of this report was to document, through a literature search, the hazards to which workers may be exposed when working with urethanes. A summary of the hazards documented in the literature and discussed in this report can be found in Table 2. Identification of a specific hazard and recommendations for action to remove the hazard must be based on a thorough study of each individual problem area. The literature review has established that, in most cases, the nature of the hazard will be a function of the specific urethane involved and conditions of use. To properly assess the magnitude of the hazard, the hazardous conditions generated by the urethane in question must be compared with the hazardous conditions which potentially could be generated by using other materials for the same application.

Table 2 - Summary of chemical hazards.

1. ISOCYANATES

A. 2,4 Toluene Diisocyanate (TDI)

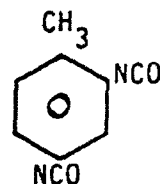
Mwt. 174.16

Mpt. 21.7°C

Bpt. 237°C

OSHA TLV* 20 ppb.

A white-water liquid with a fruity
pungent odor; turn straw-colored
on standing.

B. Diphenylmethane 4,4' Diisocyanate (MDI)
also called methylene bis phenylisocyanate.

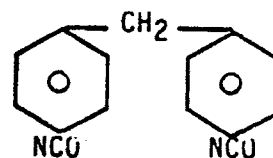
Mwt. 250.25

Mpt. 37.2°C

Bpt. 172°C

OSHA TLV 20 ppb.

Light yellow to white crystals or fused
solid, slightly soluble in water.



2. HAZARDOUS AMINES

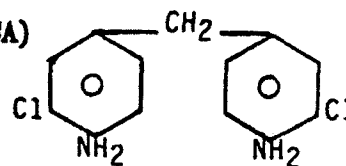
A. 4,4' Methylene bis(2-chloroaniline) (MOCA)

Mwt. 287.2

Mpt. 110°C

OSHA TLV 20 ppb.

Demonstrated carcinogenic activity in laboratory animals.



B. 2,4 Diaminotoluene

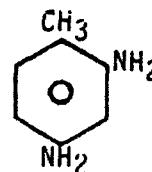
Mwt. 122.2

Mpt. 99°C

Bpt. 280°C

No established level of exposure.

Diaminotoluene is the hydrolysis product
of TDI. Demonstrated carcinogenic
activity in laboratory animals.

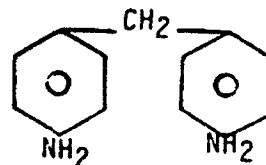


C. 4,4' Diaminodiphenyl Methane

Mwt. 198.3

Mpt. 175.7°C

Diaminodiphenyl methane is the hydrolysis
product of MDI. No established level of
exposure. Carcinogenic activity in
laboratory animals inconclusive.



(Continued)

Table 2 (continued)

3. HAZARDOUS GASES

A. Carbon Monoxide	CO
Mwt. 28 A colorless, odorless gas. Formed when urethanes burn. OSHA TLV 50 ppm.	
B. Hydrogen Cyanide	HC≡N
Mwt. 27 Gas has the odor of bitter almonds. Formed when urethanes burn. OSHA TLV 10 ppm	
C. Hydrogen Chloride	HCl
Mwt. 36.5 A colorless, corrosive, nonflammable gas, with a pungent odor. Formed when urethanes burn. OSHA TLV 5 ppm	

*TLV - Threshold limiting value. Ten-minute exposure level not to be exceeded.

While specific recommendations are beyond the scope of this review, some generalizations concerning chemical hazards in work areas can be described. The following are work areas in which hazards may be present:

- Workers involved with the fabrication of component parts from urethanes (mixing, molding, and curing operations). Airborne isocyanates and MOCA are potential hazards of which that workers must be aware.
- Workers involved with the grinding, sanding, or milling of urethane components or slabstock. Airborne isocyanates and urethane dust are potential hazards of which that workers must be aware.
- A potential fire hazard exists with all urethane materials. When a source of thermal energy is present [open flame (welding torch), resistance heater, high-energy radiation source (UV lamp), or general-purpose heating ovens], all workers must be aware of the potential for a fire and the hazardous gases (HCN & CO) and smoke that can result from the thermal decomposition of urethanes.

Workers in areas of the type described above should be informed of the hazard potential by the employer and educated in the safe use and handling of the materials involved. Government publications are available that describe safe use and handling procedures for most hazardous materials associated with the manufacture of urethanes. For example, NIOSH publication, "A Recommended Standard for Occupational Exposure to Diisocyanates" [6] discusses such topics as workplace air standards, medical surveillance, warning signs, an employee education program, safe work practices, sanitation, and personal protective equipment and clothing, as they apply to worker exposure to isocyanates.

With respect to protective equipment and clothing, the following recommendations are given for workers exposed to isocyanates:

- Eye Protection: The employer shall provide face shields with goggles.
- Skin Protection: The employer shall provide appropriate protective clothing that is resistant to penetration by isocyanates (rubber or polyvinyl chloride), to include such items as gloves, aprons, suits, and boots. Protective clothing shall be cleaned, inside and out, after each use.
- Respiratory Protection: When use of a respirator is permitted and where concentration levels of air-borne isocyanates dictate use, a respirator of appropriate design must be supplied. For example, when air-borne isocyanate levels less than 1,000 ppb are likely to be encountered, a Type C supplied-air respirator with full facepiece, helmet, or hood operated in continuous flow mode is recommended.

As previously stated, an appropriate response to a hazardous condition must be evaluated in terms of the specific urethane involved and conditions of use. For isocyanates, the type and nature of safety equipment supplied depends upon the concentration and physical form of the isocyanate (solid, liquid, or gas--mist) to be encountered in the workplace.

PERSPECTIVE

The findings of this review can be put into perspective by quoting from a study of relative toxicity conducted by Levin [25,26] using the NBS toxicity test at the NBS Fire Research Center. "The relative toxicity of different cellulosic and polymeric materials, including rigid and flexible urethane foam has been evaluated using the NBS toxicity test method. The data indicates that the combustion products from rigid urethane fall within the toxicological range of a wide variety of other products. Comparison of toxicity test values for rigid urethane with corresponding values for Douglas fir and flexible urethane foam suggests that rigid urethane is two to three times more toxic in the flaming mode than in the non-flaming mode. The difference, however, is less than an order of magnitude and is not considered toxicologically significant."

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